Materials Science Forum
ISSN: 0255-5476, Vol. 846, pp 539-544
doi:10.4028/www.scientific.net/MSF.846.539

Submitted: 2015-01-08
Revised: 2015-04-16
Accepted: 2015-04-20

Characterization of Proton Conducting Carboxymethyl cellulose/Chitosan Dual-blend Based Biopolymer Electrolytes

M.S.A. Rani[1,a], N.S. Mohamed[2,b], M.I.N. Isa[3,c*]

[1]Institute of Graduate Studies, University of Malaya, 50603 Kuala Lumpur, Malaysia

[2]Centre for Foundation Studies in Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

[3]Centre for Corporate Communication and Image Development, Universiti Malaysia Terengganu, 21300 Kuala Terengganu, Terengganu, Malaysia

[a]iker.asmal55@gmail.com, [b]nsabirin@um.edu.my, [c]ikmar_isa@umt.edu.my

Keywords: Carboxymethyl cellulose, chitosan, biopolymer electrolytes, dual-blend.

Abstract. This article presents the discovery on biopolymer electrolytes comprising of ammonium nitrate, NH4NO3 with dual-blend biopolymer materials, carboxymethyl cellulose/chitosan which were prepared via solution-casting technique. The biopolymer blend based electrolyte films were characterized by Fourier Transform Infrared spectroscopy to investigate the formation of the dual-blend biopolymer based complexes. X-Ray Diffraction result showed that all dual-blend samples were predominantly amorphous. Electrochemical impedance spectroscopy was conducted to obtain their ionic conductivities. The highest conductivity at ambient temperature of 1.03 × 10–5 S cm–1 was obtained for the electrolyte film containing 40 wt% of NH4NO3. These results indicated that the dual-blend biopolymer based electrolyte has potential for application of electrochemical devices.

Introduction

Solid polymer electrolytes (SPEs) are of immense interest as potential components in storage devices such as batteries and smart windows [1] due to their low cost of production, remarkable properties of free from volatile as well as their potential flexibility and moladability. SPEs also possess the advantage of their unique properties such as ease of fabrication into thin film with large surface area to give high energy density, ability to accommodate a wide range of ionic salts doping compositions, good electrode-electrolyte contact and high ionic conductivity [2]. Furthermore, the use of all solid polymer electrolytes would overcome the limitations of liquid electrolytes, negate the need of separator and be processed easily [3]. Polymer blends have received great interest in recent years as it is an economical technique to develop new polymeric materials with superior properties. It is the cheapest and easiest to obtain new polymeric materials compared to developing new polymers. However, the properties of materials produced by this technique depend on the degree of miscibility of the polymers [4]. No phase separation between the two polymers indicates that the blends are miscible [5]. Besides that, it has been reported that the polymer blend electrolytes exhibited high conductivity [6,7] and good mechanical strength [8-10].

Currently, most of host polymer investigated are petroleum based polymers which are non-biodegredable and harmful to our environment. Natural polymers such as cellulose, chitin, starch and chitosan for example act as alternative materials to commercially available petroleum based polymers. Carboxymethyl cellulose (CMC) and chitosan (CS) are abundantly available polymers which have good film forming property, can form transparent films and possess good mechanical strength [11]. Both polymers are non-toxic, renewable, biocompatible and biodegradable [12]. CMC contains a hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups, and hence shows amphiphilic characteristic. In general, cellulose is made up of glucose rings connected by –C(1)–O–C(4) ether bonds known as β-1,4 glycosidic linkages with extensive intramolecular hydrogen [13,14]. Meanwhile, CS is one of the polymer that has a high degree of N-deacetylated form of chitin; a naturally abundant mucopolysaccharide that serves as supporting material of

crustaceans, insects and others [15]. Chitosan is an odourless, flabby powder or flake whose color varies from yellow to white, that can be easily dissolved in some inorganic and organic acids. It has numerous unique properties include polyoxysalt formation, ability to form films, chelate many metal ions, contain reactive amino and hydroxyl groups and possess novel optical and structural characteristics [16] that make chitosan a good host polymer for solid state electrolyte. Besides that, it is insoluble in either water or organic solvents and can be dissolved in hydrochloric acid and aqueous organic acids such as formic, acetic, oxalic, and lactic acids. The solubility of chitosan depends on the concentration and type of acid.

In this work, the structural, amorphousity, and electrical properties of biopolymer dual-blend, CMC/CS impregnated with ammonium nitrate have been investigated. These biopolymer blend electrolytes are hoped can replace commercial polymer to sustain green world in the future.

Experimental

Sample preparation

CMC (Acros Organic Co.) and CS (W.A. Hammond Drierite Company Ltd.) were dissolved in 1% of acetic acid solution. Solution casting technique was employed to obtain -films with varied amount of ammonium nitrate concentration (10-50 wt. %). Pure dual-blend film without dopant was also prepared as a control. In a clean beaker, weighted amounts of CMC and CS powder with 2:1 ratio with NH_4NO_3 crystals (purity 99%) were dissolved in 100 ml of 1% acetic acid at room temperature. Complete dissolution was achieved after 24 hours stirring at room temperature using magnetic stirrer. The final light yellowish solution was then poured into separate Petri dishes and left to dry in an oven to form yellowish transparent thin films. Dual-blend biopolymer electrolyte films were transferred to a desiccator for further drying prior to characterization. Fig. 1 shows the photograph of yellowish-transparent film of CMC/CS-NH_4NO_3 biopolymer electrolyte.

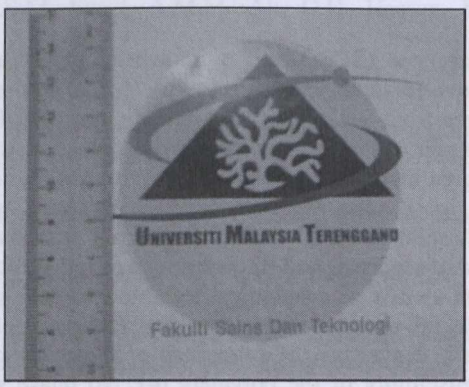

Fig. 1 Photograph of yellowish-transparent film of CMC/CS-NH_4NO_3 biopolymer electrolyte.

FTIR spectroscopy. The FTIR measurement was performed by using Thermo Nicolet 380 FTIR spectrometer equipped with an Attenuated Total Reflection (ATR) accessory and a germanium crystal. The samples were placed onto germanium crystal and infrared light will be passed through the sample in the range of 700 cm^{-1} to 4000 cm^{-1} with spectra resolution of 4 cm^{-1} at room temperature. The FTIR data were recorded in the transmittance mode.

X-ray diffractometer analysis. XRD patterns were recorded on a Rigaku MiniFlex II Diffractometer. Samples were cut into a suitable size and then adhered onto a glass sample holder. The glass sample holder was then attached to the diffractometer and the samples were directly scanned at 2θ angles between 5° and 80° at room temperature. XRD was performed to determine the nature of the biopolymer electrolytes whether crystalline, amorphous or both.

Impedance spectroscopic study. The impedance study was performed by using Hioki 3532-50 LCR Hi-Tester. Impedance data were collected for the frequency ranging from 50 to 1 MHz. Impedance spectroscopic measurement was performed to determine the ionic conductivity of biopolymer electrolyte films over a temperature range from 30 to 100 °C. The biopolymer electrolyte sample were sandwiched between stainless steel electrodes which have a surface contact area of 2.0 cm^2 and the samples were mounted onto the sample holder under spring pressure.

Results and discussion

FTIR spectroscopy. The FTIR spectra of the dual-blend biopolymer system change according to their composition and may be able to show the occurrence of complexation and interaction between the various constituent. Fig. 2 reveals that IR-spectrum of dual-blend film, CMC/CS doped with NH_4NO_3 (NH_4NO_3 (10-40 wt%) in the spectral range from 700 cm^{-1} to 2000 cm^{-1}. Upon addition of NH_4NO_3 concentration, the intensity of CMC/CS peak becomes less obvious. The NH_4NO_3 molecules which are relatively small compared to polymer molecules penetrate into CMC/CS matrix and establish attractive forces between NH_4NO_3 molecules and chain segment. These attractive forces reduce the cohesive force between the polymer chains and increase the segmental mobility [1].

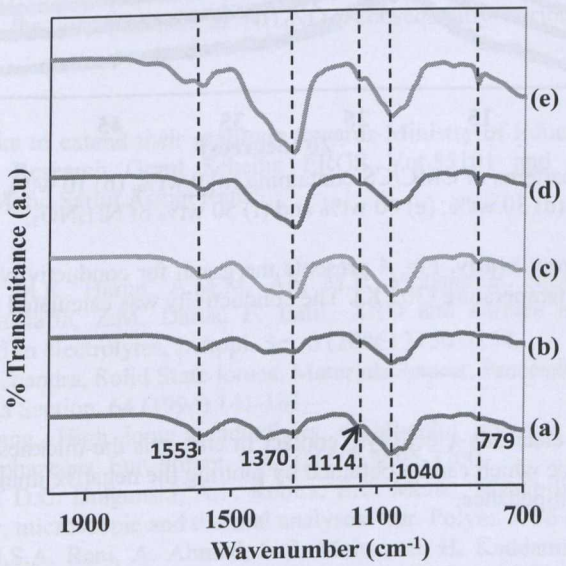

Fig. 2 IR-spectra of dual-blend CMC/CS doped with (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, (d) 40 wt%, and (e) 50 wt% of NH_4NO_3.

The band at 1553 cm^{-1} confirmed the presence of COO^- and assigned to stretching of the carboxyl group. The assignment of the 1553 cm^{-1} to the asymmetrical COO^- stretching indicates that chitosan and acetic acid have formed a chitosan–acetic acid salt. Upon addition of NH_4NO_3 salt, the gap between the carbonyl and amine bands is observed to increase up to 97 cm^{-1}. According to Rinaudo et al. [17], the cation of the acetic acid interacts with the nitrogen atom of the amine group. This leads to a shift of the amine and other bands as well. The bands observed at 1425 and 1370 cm^{-1} were assigned to $-CH_2$ scissoring and –OH bending vibration of CMC [14]. The bands at 1114 and 1040 were characteristics of the C-O stretching on polysaccharide skeleton [18]. A new peak is observed at 779 cm^{-1}. This peak is corresponds to the symmetric bending mode of NO_3^- and is observed to grow with increase in NH_4NO_3.

X-ray diffraction analysis. Fig. 3 presents the XRD patterns of dual-blend films of CMC/CS containing 0 to 50 wt% of NH_4NO_3. The XRD analysis reveals that the complex formation in the polymer matrices and shows that all samples are mostly amorphous. Upon addition of the NH_4NO_3 salt, the diffraction peak centered at ~21° becomes broaden and shifted to the higher Bragg's diffraction angle. These changes can be caused by the increase of interaction of the ionic dopant with the polymer that results in the increase of amorphousness in the CMC/CS-NH_4NO_3 biopolymer blend system [19, 20]. This proves that the addition of NH_4NO_3 helps to generate more amorphous region and disrupted the semi-crystalline region in the dual-blend CMC/CS systems.

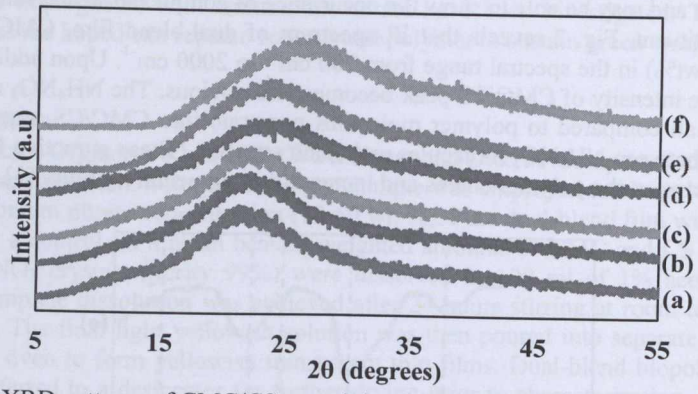

Fig. 3 XRD patterns of CMC/CS containing (a) 0 wt%, (b) 10 wt%, (c) 20 wt%, (d) 30 wt%, (e) 40 wt% and (f) 50 wt% of NH_4NO_3.

Impedance Spectroscopy Study. Fig. 4 presents the graph for conductivity against concentration of NH_4NO_3 at ambient temperature (303 K). The conductivity was calculated using:

$$\sigma = \frac{t}{R_b A} \tag{1}$$

where A is the area of electrode–electrolyte contact in cm^2, t is the thickness of the sample in cm and R_b is bulk resistance which can be obtained by plotting the negative imaginary impedance, $-Z_i$, versus real part, Z_r, of impedance.

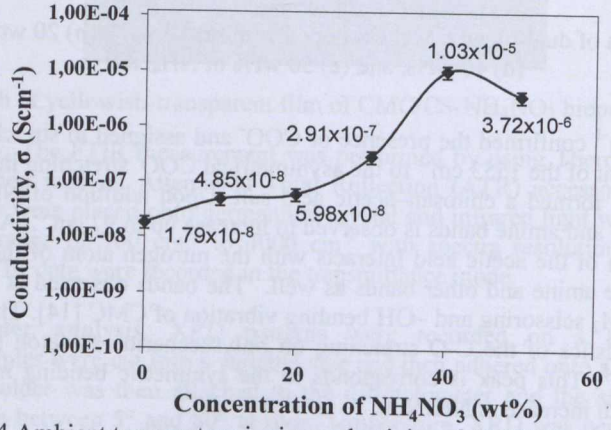

Fig. 4 Ambient temperature ionic conductivity of CMC/CS-NH_4NO_3.

From Fig. 4, pure polymer blend (NH_4NO_3-0 sample) indicates the ionic conductivity of 1.79 x 10^{-8} S cm^{-1}. The conductivity increases from the addition of 10 until 40 wt% of NH_4NO_3. As the salt composition increases, more protons (H^+) are supplied due to the dissociation of the ionic dopant. The maximum ionic conductivity achieved is 1.03 x 10^{-5} S cm^{-1}. The increase of ionic conductivity with addition of NH_4NO_3 concentration is due to the increase of the number of charge carrier and mobility of ions/conducting species [21]. However, the conductivity dramatically declines after addition of 40 wt% NH_4NO_3. Ng and Mohamad [22] reported that as NH_4NO_3 concentration increases, the host matrix (polymer blend) becomes more crowded with the dopant ions. Hence, reduces the transportation of charge carriers due to limitation of ionic mobility [23].

Summary

Biopolymer dual-blend based CMC and CS incorporated with NH_4NO_3 were prepared and characterized. The obtained results revealed that the NH_4NO_3 influence the ionic conductivity of the biopolymer blend electrolytes and the best value of 5.77 × 10–5 S cm–1 was obtained for the system containing 40 wt% of NH4NO3 at ambient temperature. This is attributable to the increase in the number of ions in the system. IR spectra provides insight into the possible interaction occur upon the addition of NH_4NO_3 with CMC. XRD studies reveal that the increase in the amorphosity of all samples upon the incorporation of NH_4NO_3, consequently attributed to the increase in conductivity.

Acknowledgments

The authors would like to extend their gratitude towards Ministry of Education (MOE), Malaysia for the Exploratory Research Grant Scheme ERGS Vot.55101 and the scholarship under MyBrain15 given to Mohd Saiful Asmal Rani.

References

[1] M.Z.A. Yahya, M.K. Harun, A.M.M. Ali, M.F. Mohammat, M.A.K.M. Hanafiah, S.C. Ibrahim, M. Mustaffa, Z.M. Darus, F. Latif, XRD and surface morphology studies on chitosan-based film electrolytes, J. Appl. Sci. 6 (2006) 3150-3154.

[2] S. Chandra, A. Chandra, Solid State Ionics: Materials Aspect. Proceedings-National Academy of Sciences India Section. 64 (1994) 141-181.

[3] S. Zhou, S. Fang, High ionic conductivity of all-solid polymer electrolytes based on polyorganophosphazenes. Eur. Polym. J. 43 (2007) 3695-3700.

[4] S.M.D.S. Neiro, D.C. Dragunski, A.F. Rubira, E.C. Muniz, Miscibility of PVC/PEO blends by viscosimetric, microscopic and thermal analyses. Eur. Polym. J. 36 (2000)583-589.

[5] S. Rudhziah, M.S.A. Rani, A. Ahmad, N.S. Mohamed, H. Kaddami, Potential of blend of kappa-carrageenan and cellulose derivatives for green polymer electrolyte application. Ind. Crop. Prod. (2015). (doi:10.1016/j.indcrop.2014.12.051)

[6] R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T. Hattori, Conductivity and thermal studies of blend polymer electrolytes based on PVAc–PMMA. Solid State Ionics 177 (2006) 2679-2682.

[7] M. Sivakumar, R. Subadevi, S. Rajendran, H.C. Wu, N.L. Wu, Compositional effect of PVdF–PEMA blend gel polymer electrolytes for lithium polymer batteries. Eur. Polym. J. 43 (2007) 4466-4473.

[8] H.S. Han, H.R. Kang, S.W. Kim, H.T. Kim, Phase-separated polymer electrolyte based on poly (vinyl chloride)/poly (ethyl methacrylate) blend. J. Power Sources 112 (2002) 461-468.

[9] L. Fan, Z. Dang, C.W. Nan, M. Li, Thermal, electrical and mechanical properties of plasticized polymer electrolytes based on PEO/P (VDF-HFP) blends. Electrochim. Acta 48 (2002) 205-209.

[10] S. Ramesh, T. Winie, A.K. Arof, Investigation of mechanical properties of polyvinyl chloride–polyethylene oxide (PVC–PEO) based polymer electrolytes for lithium polymer cells. Eur. Polym. J. 43 (2007) 1963-1968.

[11] H. Huang, P. He, N. Hu, Y. Zeng, Electrochemical and electrocatalytic properties of myoglobin and hemoglobin incorporated in carboxymethyl cellulose films. Bioelectrochemistry 61 (2003) 29-38.
[12] M.P. Adinugraha, D.W. Marseno, Synthesis and characterization of sodium carboxymethylcellulose from cavendish banana pseudo stem (Musa cavendishii LAMBERT). Carbohyd. Polym. 62 (2005) 164-169.
[13] M.S.A. Rani, S. Rudhziah, A. Ahmad, N.S. Mohamed, Biopolymer Electrolyte Based on Derivatives of Cellulose from Kenaf Bast Fiber. Polymers, 6(2014), 2371-2385.
[14] D.R. Biswal., R.P. Singh, Characterisation of carboxymethyl cellulose and polyacrylamide graft copolymer. Carbohyd. Polym. 57 (2004) 379-387.
[15] S.S. Alias, S.M. Chee, A.A. Mohamad, Chitosan–ammonium acetate–ethylene carbonate membrane for proton batteries. Arab J. Chem. In Press Accepted Manuscript (2014). (doi:10.1016/j.arabjc.2014.05.001).
[16] P.G. Seferian, M.L. Martinez, Immune stimulating activity of two new chitosan containing adjuvant formulations. Vaccine 19 (2000) 661-668.
[17] M. Rinaudo, G. Pavlov, J. Desbrieres, Influence of acetic acid concentration on the solubilization of chitosan. Polymer 40 (1999) 7029-7032.
[18] A.S. Samsudin, E.C.H. Kuan, M.I.N. Isa, Investigation on the potential of proton conducting biopolymer electrolytes based methyl cellulose-glycolic acid. Int. J. Phys. Sci. 16 (2011) 477-485.
[19] A.S. Samsudin, W.M. Khairul, M.I.N. Isa, Characterization on the potential of carboxy methylcellulose for application as proton conducting biopolymer electrolytes. J. Non-Cryst. Solids 358 (2012) 1104-1112.
[20] S. Rudhziah, N.S. Mohamed, Characterization of Proton Conducting PVDF-HFP/PEMA Blend Based Solid Electrolytes. Solid State Science and Technology 17 (2009) 73-80.
[21] M.S.A. Rani, N.A. Dzulkurnain, A. Ahmad, N.S. Mohamed, Conductivity and Dielectric Behavior Studies of Carboxymethyl Cellulose from Kenaf Bast Fiber Incorporated with Ammonium Acetate-BMATFSI Biopolymer Electrolytes. Int. J. Polym. Anal. Ch. 20 (2015) 250-260.
[22] L.S. Ng, A.A. Mohamad, Protonic battery based on a plasticized chitosan-NH4NO3 solid polymer electrolyte. J. Power Sources 163 (2006) 382-385.
[23] M.L.H. Rozali, A.S. Samsudin, M.I.N. Isa, Ion conducting mechanism of carboxy methylcellulose doped with ionic dopant salicylic acid based solid polymer electrolytes. Int. J. App. Sci. Tech. 2 (2012) 113-121.